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Review

Using Additives to Control the Decomposition Temperature of Sodium Borohydride

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Abstract

Hydrogen (H_2) shows great promise as zero-carbon emission fuel, but there are several challenges to overcome in regards to storage and transportation to make it a more universal energy solution. Gaseous hydrogen requires high pressures and large volume tanks while storage of liquid hydrogen requires cryogenic temperatures; neither option is ideal due to cost and the hazards involved. Storage in the solid state presents an attractive alternative, and can meet the U.S. Department of Energy (DOE) constraints to find materials containing > 7 % H_2 (gravimetric weight) with a maximum H_2 release under 125 °C.

While there are many candidate hydrogen storage materials, the vast majority are metal hydrides. Of the hydrides, this review focuses solely on sodium borohydride ($NaBH_4$), which is often not covered in other hydride reviews. However, as it contains 10.6% (by weight) H_2 that can release at 133 ± 3 $JK^{-1}mol^{-1}$, this inexpensive material has received renewed attention.

$NaBH_4$ should decompose to H_2(g), Na(s), and B(s), and could be recycled into its original form. Unfortunately, metal to ligand charge transfer in $NaBH_4$ induces high thermodynamic stability, creating a high decomposition temperature of 530 °C. In an effort make H_2 more accessible at lower temperatures, researchers have incorporated additives to destabilize the structure.

This review highlights metal additives that have successfully reduced the decomposition temperature of $NaBH_4$, with temperatures ranging from 522 °C (titanium (IV) fluoride) to 379 °C (niobium (V) fluoride). We describe synthetic methods employed, chemical pathways taken, and the challenges of boron derivative formation on H_2 cycling. Though no trends can be found across all additives, it is our hope that compiling the data here will enable researchers to gain a better understanding of the additives' influence and to determine how a new system might be designed to make $NaBH_4$ a more viable H_2 fuel source.

Keywords

borohydride; $NaBH_4$; hydrogen storage; additives; energy; dehydrogenation

1. Introduction

There is an ever increasing need to develop energy efficient materials that are environmentally friendly. Hydrogen (H_2) burned with oxygen is incredibly clean, and is becoming a popular zero-carbon emission fuel. Unfortunately, the storage of pure H_2 can be problematic. Storing in its gaseous state is very common, but there are serious concerns about flammability and explosive hazards. Storing H_2 in the liquid state requires ultralow, cryogenic temperatures, making storage expensive while adding the hazards, challenges and expense of cryogen handling [1, 2]. There is a strong need to create a regenerative hydrogen storage material that is safe and lightweight enough for easy transportation. Thus, researchers have been exploring H_2 storage methods in the solid state, trying to meet the constraints given by the U.S. Department of Energy (DOE) [3], such as the recommendation to find materials containing > 7 % H_2 (gravimetric weight) with a maximum H_2 release rate under 125 °C.

There have been various strategies employed to develop these solid state materials. Some have focused on H_2 adsorbents, gaining an understanding of the gravimetric and volumetric capacities and binding strengths in materials such as metal organic and covalent organic frameworks [4]. Interestingly, there is often disagreement in this field on the theoretical analysis, such as calculating the H_2 capacity. Other researchers have turned their attentions toward nanostructured hydride materials, whose tiny size and large surface area make it possible to tune its properties independently of their bulk counterparts [5]. Research is ongoing, and it remains to be determined whether the required thermodynamics can be achieved to make metal hydrides a viable H_2 storage material, especially considering that hydrogenation induces mechanical stresses due to volume expansion.

Four different strategies have been applied over the years to reduce the decomposition temperatures of metal hydrides: 1) The nanoconfinement approach, where the complex size is reduced by infiltration into a nanoporous scaffold, decreases the decomposition temperature as a

result of an increase of the reaction kinetics [6-9]. 2) Thermodynamic destabilisation uses additives to alter the decomposition pathway, therefore reducing the decomposition temperature. These additives may include a metal hydride, a complex metal hydride, a metal, or even a metal based compound such as a metal oxide [10, 11]. 3) Using a combination of scaffolds can both nanoconfine and thermodynamically destabilise the infiltrated complex metal hydride [12-15]. 4) Finally, the use of a catalyst increases the reaction kinetics of the metal hydrides, resulting in a lower decomposition temperature [16, 17].

This review focuses solely on a complex metal hydride system in the metal borohydride family. Sodium borohydride ($NaBH_4$) is a stable, inexpensive solid containing 10.6% (by weight) H_2 that has been a popular material of study for energy applications [18-23]. At the start of the century, scientists attempted to make use of a hydrolysis process to make $NaBH_4$ a feasible H_2 source. The clean concept was to simply react $NaBH_4$ with water via the following reaction [24]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

where the sodium metaborate ($NaBO_2$) could eventually be recycled back into $NaBH_4$ by using a catalyst such as magnesium hydride [25, 26]. Unfortunately, this process met with multiple failures due to solubility issues and low yields, so was abandoned by the DOE in 2007 [27, 28].

In more recent years, researchers have turned to non-aqueous, solid state methods to generate H_2 from $NaBH_4$. When heated, $NaBH_4$ releases 133 ± 3 J K^{-1} mol^{-1} of H_2 along with solids of sodium (Na) and boron (B), with a small amount of sodium borides and sodium hydride [2]. Furthermore, the bulk of the decomposed by-product is recyclable according to theoretical calculations, where the solids remaining after dehydrogenation can reform $NaBH_4$ via the addition of more H_2 gas:

$$Na(s) + B(s) + 2H_2(g) \rightarrow NaBH_4(s)$$

Unfortunately, the metal to ligand charge transfer in $NaBH_4$ induces high thermodynamic stability [29], so $NaBH_4$ does not decompose until about 535 °C at 1 bar of H_2 [2, 30]. This is significantly higher than the desired <125 °C proposed by the DOE. As a result, research efforts have turned toward developing methods to weaken the $NaBH_4$ structure by using additives to destabilize the bonds and decrease the temperature of decomposition, thereby making H_2 more accessible. For example, using zirconium chloride [31] or titanium fluoride [32] as additives reduces the onset temperature of dehydrogenation to about 300 °C, while cobalt, copper and nickel nanoparticles reduce this onset to as low as 200 °C [9, 17, 33, 34]. Unfortunately, dehydrogenation starting at such low temperatures is not a guarantee that the sample will decompose and completely release large amounts of H_2 at low enough temperatures to become an acceptable fuel source. Regardless, many researchers' results show promise for the method of using additives to destabilize $NaBH_4$, and there is a need for ongoing work to develop a better understanding of how additives incorporate into $NaBH_4$ in order to improve future materials design.

Figure 1 compiles the known decomposition temperatures of $NaBH_4$ resulting from the use of various additives. Though there are no obvious trends for controlling decomposition through metal size, anion selection, oxidation state, etc., there is a wide range of accessible decomposition

temperatures available using additives to lower the kinetics. Current methods have been able to reduce the decomposition temperature as low as 379 °C. Though this does not quite reach the targets set by DOE, $NaBH_4$ may still be a relevant H_2 storage material if a better additive can be found.

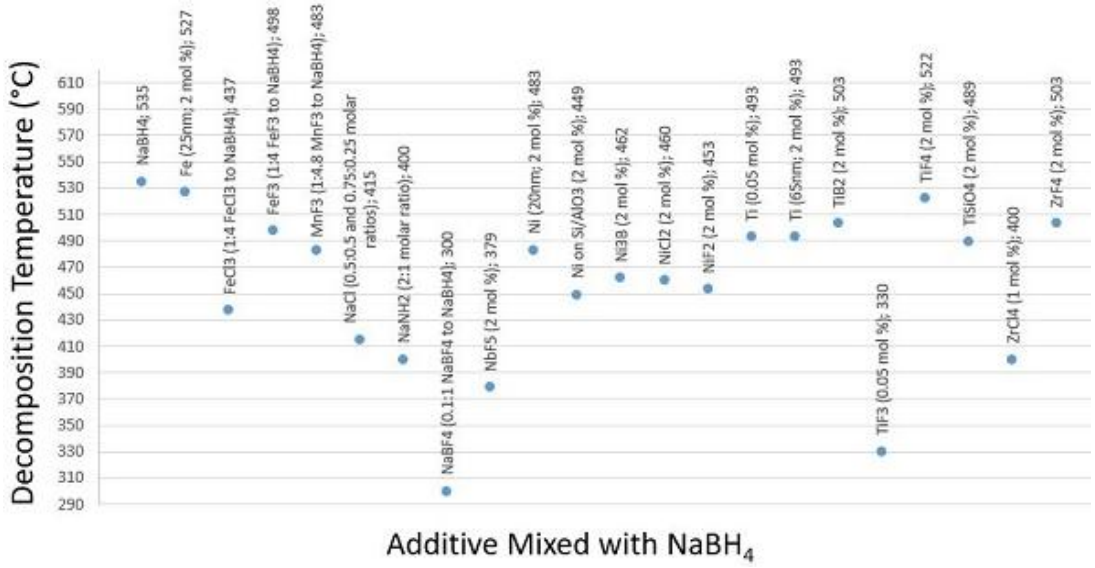

Figure 1 Compiled onset decomposition temperatures of $NaBH_4$ with additives, listing additive; decomposition in °C [15, 30-33, 35-45]. Note that the method of data collection varies between samples, which influences the onset decomposition temperature.

The aim of this review is to provide information about recent research involving various additives to improve the kinetics of $NaBH_4$ for hydrogen storage, focusing only on additives that have been found to successfully decrease the decomposition temperature of $NaBH_4$. Note that publications reporting only the H_2 release temperature without mention of decomposition are not included in this review. Though we have made every effort to capture all relevant research, the findings here are not exhaustive. This work is organized in sections by metal additive, explaining how the various additives destabilize and reduce the decomposition temperature of $NaBH_4$. All of the research presented here used ball milling (BM) as the driving force to incorporate additives with $NaBH_4$. Interestingly, the experimental methods for both synthesis and decomposition analysis varied greatly between groups. The molar ratios of additives used, milling rate and total mill time, breaks taken throughout the milling process to cool the material, and in some cases post-milling heating to anneal differed , which may play a large role in why some additives cause $NaBH_4$ to decompose at a higher or lower temperature than expected. Furthermore, variances in the methods by which thermal decomposition was measured may have a significant influence on the values reported. Though it is not traditional to include a subsection on synthetic techniques in a review like this one, we felt it important in this instance. Though no one has yet tied together how these various methods influence the final decomposition temperature, it is our hope that having all of this data in one place will help researchers make future decisions regarding their methodology. Our ultimate goal is that this review will help researchers gain a better understanding of how to select additives to more effectively

weaken the bonds in $NaBH_4$, thus improving decomposition and H_2 release to make $NaBH_4$ a more viable hydrogen storage material.

2. Discussion

This review focuses on the changing decomposition temperatures of $NaBH_4$ when using the following additives to destabilize the $NaBH_4$ structure: Ti, Ni, Mn, Fe, Zr, and Na. A brief description of the synthetic methodology and a discussion of results are described below.

2.1 Titanium Additives

2.1.1 Titanium Additive Experimental Procedures

Ti has been incorporated into $NaBH_4$ through different ball milling techniques with the following methods:

- Humphries et. al. milled $NaBH_4$ with Ti (65nm), TiB_2 and $TiSiO_4$ (2 mol %) for 1 hour at 280 rpm under argon [33]. Decomposition temperature was measured by TGA: heated to 600 °C at 2°/min with Ar purge of 50 mL/min.
- Mao et. al. milled $NaBH_4$ with Ti, TiH_2 and TiF_3 (about 4:7 mol %) for 2 hours at 400 rpm under argon [32]. Decomposition temperature was measured by Sieverts apparatus: heated to 500°C at 5 °C/min.
- Jansa et. al. reported the effect of BM $NaBH_4$ with the TiF_4 (2 mol %) additive at 300 rpm under argon [30]. Decomposition temperature was measured by TGA: heated to 600 °C at 2 °C/min with Ar purge of 100 mL/min.

2.1.2 Titanium Additive Results and Discussion

Several different titanium (Ti) additives have been found to lower the decomposition temperature of $NaBH_4$, including hydrides, fluorides, and metal nanoparticles. Though there have been obvious challenges with the formation of intermediates and in developing trends to understand the influence of oxidation states, the fact is that these additives have been found to influence the decomposition and dehydrogenation.

Figure 1 shows that the lower decomposition temperature was obtained with $TiSiO_4$ (Ti^{+4}) additive, at 489 °C. Humphries et al. found that metallic Ti and Ti^{+2} in TiB_2 decompose at higher temperatures than this (493 °C and 503 °C, respectively). The powder x-ray diffraction (PXD) patterns show that the addition of $TiSiO_4$ and TiB_2 did not change the diffraction patterns of $NaBH_4$ during the BM process [33]. However, after milling there was an additional diffraction peak observed for Ti that suggested the presence of titanium metal [38]. Likewise, Mao et al. found that the TiF_3 PXD exhibited two phases [32, 38] after BM, suggesting the presence of the solid additive. Looking to the study of milled TiF_3 with $Mg(BH)_4$ [46], there was a destabilisation of $NaBH_4$ due to an interruption of its framework. Furthermore, Kalantzopoulos et al. found that the boron nuclear magnetic resonance (NMR) spectra of $NaBH_4$ with the TiF_3 additive contained $NaBF_4$ in a low ratio of 1:150 $NaBF_4$:$NaBH_4$. It was assumed that $NaBF_4$ was in the amorphous state as it was not detected by PXD. Its formation can be explained

thermodynamically during the warm-up induced by BM. This compound facilitates the dehydrogenation process, which will be discussed later, as it is an intermediate of the decomposition products NaF and H_2 [38]. Unfortunately, it is difficult to compare this additive effect to the others because the decomposition temperature is unknown. These samples are all physical mixtures, but the absence of additional PXD peaks for $TiSiO_4$ and TiB_2 indicates their possible presence in the amorphous state. Moreover, a similar reaction to the one with TiF_3 occurred during the BM using TiF_4, where $NaBF_4$ was formed [30]. Surprisingly, despite this substitution reaction, the decomposition temperature of this mixture (522°C) was only slightly lower than that of pure $NaBH_4$ (532 °C).

A first estimation of capacities is given by hydrogen desorption rate measurements at 440 °C for Ti (65 nm), TiH_2 and TiF_3. Within 400 minutes, the $NaBH_4$-Ti mixture desorbs 1.65 wt% of H_2, TiH_2 desorbs 1.85 wt%, and TiF_3 releases 3.2 wt% [32]. It should be noted that in the 20:1 mixture of $NaBH_4$:TiF_3, the first release of H_2 observed was from 300 to 360 °C, with a second step at 380 °C [32]. The more additive-concentrated sample, with a 4:1 ratio of $NaBH_4$:TiF_3, had lower release temperatures, with a first step from 220 and 320 °C and a second from 320 and 420 °C. Humphries et al. reported in-situ powder PXD patterns (Figure 2) [38]. From room temperature (RT) to 220 °C, the formation of Na_3TiF_6 was detected, whose diffraction intensity decreased until it disappeared at 320 °C, at which point NaF was formed. Thus, the two steps decomposition process of $NaBH_4$-TiF_3 are related firstly to the dehydrogenation that occurs during the Na_3TiF_6 formation, then to the decomposition of $NaBH_4$ decreased by the presence of the ternary fluoride [38]. In contrast to this, Mao et al. reported TiB_2 and NaF formation during TiH_2 and TiF_3 decomposition, which was determined to be an active species, but they made no mention of the appearance of Na_3TiF_6. They also commented that TiF_3 had better H_2 desorption and adsorption capacities compared to TiH_2 and Ti.

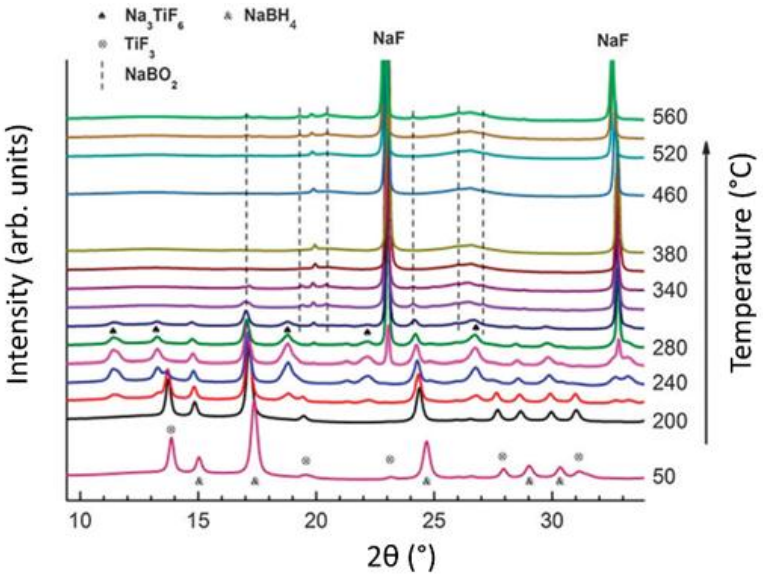

Figure 2 In-situ powder XRD of $NaBH_4$/TiF_3 system between 50 and 560 °C with a heating rate of 2 °C/min [38]. Reproduced from Ref. [38] with permission from the PCCP Owner Societies.

The thermogravimetric analysis (TGA) of a $NaBH_4$ and TiF_4 mixture indicated a mass loss of 0.3 wt% between 100 and 300 °C, and 20% between 300 and 600 °C, with H_2 desorption starting at about 470 °C [30]. It is difficult to compare TiF_4 to TiF_3 because the time exposures to temperatures were not reported, generated species were not specified in the case of TiF_4, and the ratios used differed. However, it is noteworthy that the decomposition of $NaBH_4$ with TiF_4 seemed particularly efficient, which does not contradict the observation made by Kalantzopoulos et al. about the effect of oxidation state in fluoride-containing additives.

It was observed that high oxidation states generally tend to more strongly decrease melting and decomposition temperatures. Jansa et al. [30] explained that the high coordination of the metal induced a high exchange area between $NaBH_4$ and the anions of the additive, and the additive cation furnished some vacancies that permitted further reactions. This was noticed using both chloride and fluoride additives milled with MgH_2 [47, 48]. For instance, $NaBH_4$-CeF_4 decomposed at 502 °C whereas $NaBH_4$-CeF_3 decomposed at 506 °C. Furthermore, NbF_5 (Nb^{+5}) is notably one of the best destabilizers of $NaBH_4$. However, some exceptions exist; FeF_2 and $CrCl_2$ more effectively reduce the decomposition temperature than FeF_3 and $CrCl_3$ [47]. Electronic structures of metals, depending on their oxidation state, are responsible for creating bonds during milling or heating, which influence the decomposition process. Indeed, it was highlighted earlier that TiF_3 and TiF_4 behaviours during BM, then heating, are very different. In addition, their effect on $NaAlH_4$ unit-cell dimensions also differ slightly, where the unit-cell parameter using TiF_3 is 5,0231 Å and using TiF_4 it is 5.0235 Å [49].

Ti additives offer much in the way of improving our understanding of how additives influence the decomposition of $NaBH_4$. Though the lowest decomposition temperature reported reaches only 493 °C, H_2 release has been reported in these mixed materials with an on-set temperature as low as 220 °C. There are many challenges to overcome if researchers pursue the use of Ti additives. The formation of intermediates such as Na_3TiF_6 and NaF make the chemistry of decomposition difficult to study, and raise questions about the potential for recyclability. More controlled studies are needed to gain a solid understanding of the influence of Ti oxidation states as well. The lowest reported decomposition onset temperature was 493 °C when using 65nm Ti nanoparticles as additives. Given the growing popularity of the study of nanoparticles and the well-known fact that nano-sized particles oftentimes have different tuneable properties compared to their bulk-sized counterparts, it would be worthwhile to continue this direction of research to see if smaller nanoparticles would lower the decomposition even further. It's possible that Ti will not lower the decomposition and dehydrogenation temperatures enough to be feasible for H_2 storage and transportation, but the potential insights gained about oxidation and particle size trends suggest this is a material in need of additional study.

2.2 Nickel Additives

2.2.1 Ni Additive Experimental Procedures

Nickel (Ni) additives have been studied using a traditional BM technique. Humphries et. al. has reported data for traditional milling methods using five different nickel (Ni) additives; Ni nanoparticles (20nm), Ni_3B, $NiCl_2$, NiF_2 and Ni on Si/AlO_3. A 2 molar % concentration of additives were BM at

280rpm with $NaBH_4$ under argon atmosphere for 1 hour at 280 rpm, resulting in the final mixed products [33]. The decomposition temperature was measured by TGA: heated to 600 °C at 2° /min with an Ar purge of 50 mL/min.

2.2.2 Ni Additive Results and Discussion

Unlike the Ti additive, pure nickel (Ni) nanoparticles used as traditional additives through BM do not reduce the decomposition temperature better than their halogenated counterparts. It is fortunate that BM the Ni additives with $NaBH_4$ does not result in the creation of many boron derivatives, which is promising for H_2 cyclability, but chloride additives do tend to create $Na(BH_4)_{1-x}Cl_x$. Though halogens have been mentioned, it remains to be seen how the oxidation state of Ni influences decomposition.

Both halide additives, $NiCl_2$ and NiF_2, appear to be the best destabilizers of nickel compounds just behind the mixed material Ni on Si/AlO_3. $NiCl_2$ decreases the $NaBH_4$ decomposition temperature to 460 °C and NiF_2 to 453 °C. The other additives examined, Ni_3B and Ni particles, with a much lower oxidation state (Ni^0), were nevertheless effective as they lowered the decomposition temperature of $NaBH_4$ to 462 °C and 483 °C, respectively. This temperature distribution is consistent with observations made earlier with the Ti additives with regard to oxidation states. Humphries et al.'s first PXD study affirms that no reaction took place during the BM using each Ni additive, and no borane derivatives were generated, which favours reversibility [33]. Another experiment using more concentrated samples (with 20 and 25 molar % of additive) reported substitution reactions when using chloride derivatives such as $NiCl_2$ and $TiCl_2$. The appearance of $Na(BH_4)_{1-x}Cl_x$ during BM was brought to light by PXD and FTIR [50]. This phenomena, for which the substitution ratio depends on the transition metal of the additive, has also been observed using a NaCl additive [36], which will be discussed in the sodium (Na) section below.

According to Humphries et. al., the only gas released during heating of these mixed materials was H_2. The group studied desorption by cycling pressure-composition-temperature (PCT) and found Ni_3B and $NiCl_2$ to be the most effective Ni additives (Table 1). After the first cycle, the desorption using $NiCl_2$ at 514 °C reached up to 0.25 wt%, and 1.48 wt% at the second cycle, and with Ni_3B at 460 °C the desorption was up to 1.45 wt%. It was revealed by PXD that Ni additives form Ni_3B during heating. Given the Ni_3B efficiency at destabilizing $NaBH_4$ during desorption, it was logical to observe encouraging results with other Ni components. The particular destabilizer effect of the chloride-based nickel compound could be correlated to the appearance of $Na(BH_4)_{1-x}Cl_x$ during BM, but it is not sufficient to explain its best hydrogen desorption during the second cycle. Nevertheless, $NiCl_2$ seems to show the most promise for H_2 storage applications, but with the disadvantage that it desorbs only at high temperatures. On the other hand, NiF_2 is advertised as being less effective but it has been analysed at a temperature 50 °C lower than that of chloride whereas $NaBH_4$-NiF_2 has just a 7 °C lower decomposition temperature. Furthermore, after a few dehydrogenation/rehydrogenation cycles, formation of metallic Na from the decomposition of $NaBH_4$ and NaH from the hydrogenation of metallic Na were observed in each case. The general results of Humphries et al. showed that chloride

and boride are better than fluoride additives in decreasing the decomposition temperature of $NaBH_4$, as observed in Figure 1.

Table 1 Pressure-composition-temperature hydrogenation and dehydrogenation cycling of $NaBH_4$ milled with additives Ni, $NiCl_2$, Ni on Si/Al_2O_3, Ni_3B, and NiF_2 [33].

	Ni		**$NiCl_2$**		**Ni (65 wt %) on Si/Al_2O_3**		**Ni_3B**		**NiF_2**	
Cycle	desorb 490 °C	absorb 427 °C	desorb 514 °C	absorb 430 °C	desorb 494 °C	absorb 430 °C	desorb 460 °C	absorb 414 °C	desorb 460 °C	absorb 300 °C
1	0.25	0.09	0.25	0.06	0.23	0.07	1.45	0.41	0.16	0
2	0.17	0.35	1.48	0.47	0.17	0.39	0.28	0.03	0.03	0.02
3	0.05	0.97	0.05	0.33	0.07	0.06	0.04	0.33	0.02	0.04
4	0.02	0.20	0.03	0.08	0.03	0.30	0.05	0.21	0.02	0

Desorption undertaken under initial vacuum. Absorption undertaken at ~100 bar H_2.
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It is fortunate that heating $NaBH_4$-Ni mixtures produce very few boron derivatives. Though this is promising for recyclability, there are many challenges yet to overcome. For example, fluorinated Ni reduces the decomposition temperature but increases the H_2 desorption temperature. There is also a need to study $NaBH_4$ systems with varying Ni oxidations states, as this property may be important in lowering dehydrogenation, but has yet to be studied. Additional work is needed and encouraged to determine whether Ni additives may be the key to making H_2 more accessible in $NaBH_4$.

2.3 Manganese and Iron Additives

2.3.1 Mn and Fe Additive Experimental Procedures

Several groups have studied Mn and Fe as additives with $NaBH_4$. Below are the methods that have been successful in reducing the $NaBH_4$ decomposition temperature:

- Humphries et al. ball-milled 25nm Fe nanoparticles for 1h at 280 rpm in a 2 molar % proportion with $NaBH_4$ [33]. Decomposition temperature was measured by TGA: heated to 600 °C at 2 °/min with Ar purge of 50 mL/min.
- Jansa et al. took a different approach and BM $FeCl_3$ with $NaBH_4$ in the ratio 1:4 under argon during 3 hours, with 1:100 powder to stainless balls ratio, and $MnCl_2$ was BM under the same conditions with an additive/$NaBH_4$ ratio of 1:3 [50]. Decomposition temperature was measured by TGA: heated to 600 °C at 2 °/min with Ar purge of 50 mL/min.
- Kalantzopoulos et al. also incorporated Fe additives, where $4NaBH_4$:$1FeF_3$ and $4.8NaBH_4$:$1MnF_3$ were BM at 400 rpm under argon for 3 hours, under 1 bar of argon gas [38]. Decomposition

temperature was determined via TGA by heating the sample between 30 and 600 °C with a heating rate of 21 °C and an argon gas flow of 50 mL/min.

- Sing et al. stirred $MnCl_2$ with a mortar and pestle with $NaBH_4$ in 20ml diethyl ether for 1 hour at 35 °C under nitrogen gas until the solvent evaporates totally. $MnCl_2$ was used in 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt% proportion in $NaBH_4$ [39]. The decomposition temperature was measured by TGA heating from ambient to 300 °C with a heating rate of 5 °C/min under a nitrogen gas flow rate of 50 mL/min.

2.3.2 Mn and Fe Additive Results and Discussion

Similar to what was discussed above, manganese (Mn) and iron (Fe) additives also generate boron derivatives during the milling process, and the use of chloride-based additives produces the same substituted $Na(BH_4)_{1-x}Cl_x$ structure reported for $NiCl_2$, $TiCl_2$ and NaCl. While these intermediates may pose problems for H_2 cycling, they also offer another means of reducing the decomposition and dehydrogenation temperatures of $NaBH_4$.

Kalantzopoulos et al. found that a portion of MnF_3 was reduced into MnF_2, which lead to the formation of $NaBF_4$ during milling with $NaBH_4$ [38]. Boron NMR showed a $NaBH_4$/$NaBF_4$ ratio of 40:1. The same product was generated in a higher amount ($10NaBH_4$:$NaBF_4$) when FeF_3 was used, but in an amorphous state undetectable by PXD. In the latter case, FeF_3 was reduced to metallic Fe, which led to the formation of NaF. The presence of $NaBF_4$ in the MnF_2 sample induced an overlap marked by an asymmetry of the melting peak of the differential scanning calorimetry (DSC) pattern [30]. This was not observed for the FeF_3 sample in which $NaBF_4$ was amorphous.

Residual gas analysis found that the sample containing Na-MnF_3 released H_2 in three steps. The hydrogen desorption started at a low temperature (135 °C) due to the high destabilization effect of MnF_2 (Figure 3) [38]. The first step occurred between 160 and 230 °C, when $NaBH_4$ reacted with MnF_2 to form the ternary fluoride $NaMnF_3$ with a release of 2.0 wt%. Then, between 230 and 280°C, 1.5 wt% was released. Finally, after 390 °C, 1.8 wt% was desorbed. For the Na-FeF_3 sample, from 161 to 350 °C, 1.7 wt% was released, with a high H_2 desorption rate between 250 and 350 °C. This was consistent with the in-situ PXD signal of $NaBH_4$ which started decreasing at 270 °C, and was followed by 1.5 wt% desorption between 350 and 490 °C. Given these dehydrogenation results, MnF_3 may be slightly better at destabilizing $NaBH_4$ than FeF_3. However, the decomposition temperatures of $NaBH_4$ with MnF_3 and FeF_3 are very similar, 483 °C and 498 °C, respectively (Figure 1).

Jansa et al. reported that during the BM of the chloride-containing metals $MnCl_2$ and $FeCl_3$, the BH_4^- ligand was partially substituted by Cl^- to form $Na(BH_4)_{1-x}Cl_x$ [50], as described for the $NiCl_2$, $TiCl_2$ and NaCl additives. The substitution was higher using $FeCl_3$ than $MnCl_2$. Nevertheless, $NaBH_4$ containing $MnCl_2$ had a lower H_2 release temperature below 230 °C. This is a result of other species being formed, such as amorphous Na–Mn-borohydride. Furthermore, this mixture desorbed a total of 5.7 wt% H_2. It was found by Singh et al. that the best concentration to lower the decomposition temperature was 20% $MnCl_2$ in $NaBH_4$, while $NaBH_4$ with $FeCl_3$ released H_2 and decomposed at 437 °C with a maximum H_2 desorption of 0.2 wt% between 50 and 600 °C. [39]

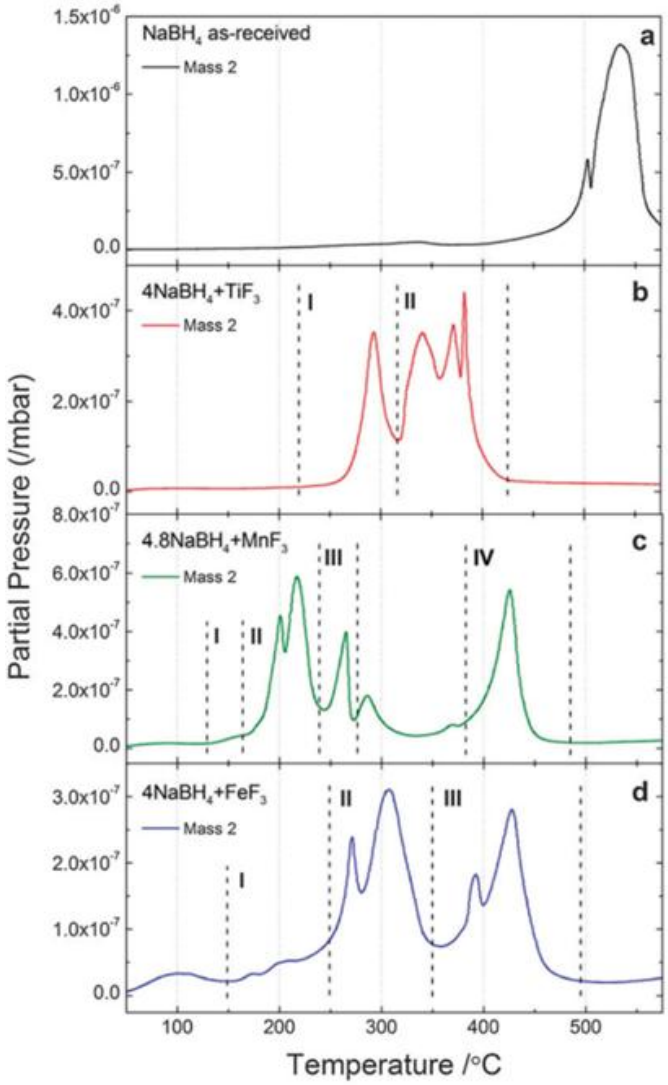

Figure 3 Temperature-programmed desorption with residual gas analysis from room temperature up to 575 °C of as-milled samples of a) pure $NaBH_4$, b) $4NaBH_4 + TiF_3$, c) $4.8NaBH_4 + MnF_3$, and d) $4NaBH_4 + FeF_3$ [38]. Reproduced from Ref. [38] with permission from the PCCP Owner Societies.

The use of Fe and Mn additives to reduce the decomposition temperature of $NaBH_4$ has meet with some success. Interestingly, when compared to Ti additives, the opposite trend of halogen size occurs, with the Cl having the lower decomposition temperature (reaching 437 °C with $FeCl_3$ and 498 °C with FeF_3). This prohibits researchers from drawing all-encompassing conclusions about halogens attached to metal additives. It's possible the trend here differs because of the multi-step process of dehydrogenation, or that the boron derivatives must be taken into account when attempting to draw conclusions about best additive selections. Additional research is needed to determine whether or not Mn and Fe additives may have a different outcome when incorporated as nanoparticles, and if other types of additives containing these metals might prevent the formation of the boron derivatives during BM.

2.4 Zirconium Additives

2.4.1 Zr Additive Experimental Procedures

Two zirconium (Zr) additives have been used in an attempt to improve the H_2 desorption of $NaBH_4$:

- Kumar et al. ball-milled $NaBH_4$ with 1 mol % $ZrCl_4$ using stainless steel balls under 0.1 MPa argon gas for two hours, with a 30 minute break to cool the sample half way through the milling process [31]. Decomposition temperature was measured by TGA: heated to 600 °C at 2 °C/min with an Ar purge of 50mL/min.
- Jansa et al. ball-milled $NaBH_4$ with 2 mol % ZrF_4 at 300rpm under an argon atmosphere for one hour [30]. Decomposition temperature was measured by TGA: heated to 600 °C at 2 °C/min with an Ar purge of 100 mL/min.

2.4.2 Zr Additive Results and Discussion

It is possible to reduce the decomposition temperature of $NaBH_4$ using halogenated Zr additives. Unlike the previous additives discussed, the chlorinated $ZrCl_4$ decomposes $NaBH_4$ at a significantly lower temperature than the fluorinated ZrF_4, with a difference of more than 100 °C. Researchers have yet to determine why the different halogens yield such drastically different outcomes, but it is promising that work has been done to determine how the BM process changes the chemistry of these additives.

Studies involving $ZrCl_4$ have found that this additive interacts with the surfaces of magnesium borohydride and magnesium hydride to improve H_2 release while reducing to $ZrCl_3$/$ZrCl_2$ and nano-sized Zr metal [51, 52]. When added into the $NaBH_4$ system, a similar change of the precursor occurs. The thermodynamic calculations of Kumar et al. discovered that $ZrCl_4$ reacts with $NaBH_4$ during BM via the following two pathways [31]:

$$4\ NaBH_4 + ZrCl_4 \rightarrow 4NaCl + 4B + Zr + 8H_2\ (g)$$
$$2\ NaBH_4 + ZrCl_4 \rightarrow 2NaCl + 2B + ZrCl_2 + 4H_2\ (g)$$

The $ZrCl_4$ reduces partially to $ZrCl_2$ and completely to metallic Zr. Kumar et. al reported that the $ZrCl_4$ additive reduces the crystallite size of $NaBH_4$ during BM, making $NaBH_4$ more reactive as a result of the increased surface area. Interestingly, though it was clear that $ZrCl_4$ reacted with $NaBH_4$, no NaCl was detected by PXD as a byproduct upon completion of the BM process. This problem with detection was either due to small concentrations or else the NaCl was amorphous, so not measurable by this technique.

TGA results comparing pure $NaBH_4$ (p-$NaBH_4$) and $ZrCl_4$-containing $NaBH_4$ (c-$NaBH_4$) are shown in Figure 4 [31]. The decomposition and dehydrogenation of the milled p-$NaBH_4$ began at 475 °C, with the sample losing more than 60% of its weight by 600 °C. This weight loss reportedly was a result of both hydrogen desorption and the evaporation of Na metal, the latter of which does not bode well for recyclability of this material. The $ZrCl_4$ additive, on the other hand, had a significant impact on the

decomposition temperature, reducing the onset temperature to below 300 °C, with most of the H_2 content being released by 500 °C.

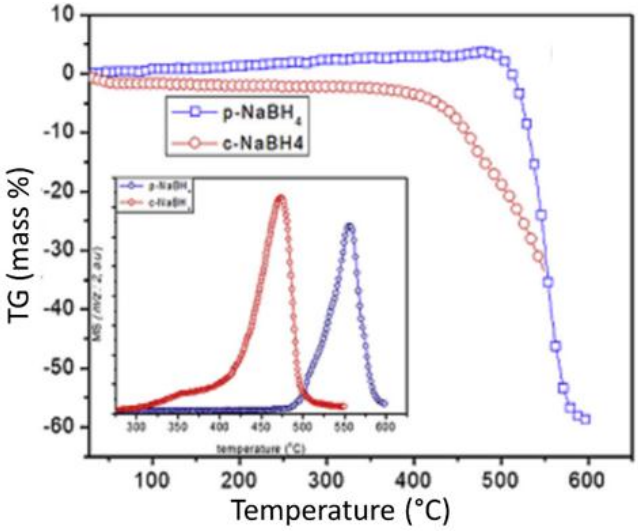

Figure 4 TGA of pure-$NaBH_4$ (p-$NaBH_4$) and $ZrCl_4$-containing $NaBH_4$ (c-$NaBH_4$) with corresponding hydrogen evolution observed by MS (inset) [31]. Reprinted from Int J Hydrogen Energ., Vol 42, Kumar S, Jain A, Miyaoka H, Ichikawa T, Kojima Y., Study on the thermal decomposition of $NaBH_4$ catalyzed by $ZrCl_4$, 22432-22437, Copyright 2017, with permission from Elsevier.

The Fourier-transform infrared spectroscopy (FTIR) data showed no changes between pure and $ZrCl_4$-containing $NaBH_4$, while x-ray photoelectron spectroscopy (XPS) confirmed that there were notable changes to the oxidation state of the Zr additive. In fact, all XPS peaks shifted to lower energy after $NaBH_4$ and $ZrCl_2$ were milled together, with energy changes of the Zr3d electrons pointing to the Zr^{4+} oxidation shifting to Zr^{2+} after the reaction. Overall, the data reported found that $ZrCl_4$ reduced to $ZrCl_2$, but it is unclear if metallic Zr was formed or if $ZrCl_2$ was in any way responsible for the effect observed.

Unlike other metal examples listed in this review, the fluorinated ZrF_4 additive did not reduce the decomposition temperature of $NaBH_4$ nearly as much as the chlorinated $ZrCl_4$, reaching only 503 °C compared to 400 °C. The ZrF_4 additive also lost its diffraction pattern after BM, corresponding to the formation of metallic Zr and $NaBF_4$. It remains to be seen if cyclability of H_2 is possible with this complex, but given the high temperature required to decompose $NaBH_4$ with ZrF_4, it is likely that this mixed material is not worth pursuing.

Boron derivatives remain an ongoing challenge in the quest to find materials that will work for H_2 cycling, and Zr additives are not immune to this problem. However, the ability of the $ZrCl_4$ additive to decrease the decomposition so low may be one of the keys to designing a better material. Though going nano in size doesn't always solve the problem, it would be interesting to see how Zr nanoparticles influence the decomposition of $NaBH_4$, and to see if more complex Zr additives have a different outcome.

2.5 Sodium Additives

2.5.1 Na Additive Experimental Procedures

Several groups have reported the use of Na additives with $NaBH_4$, with varying results as to changes in decomposition. Below are the methods reported that were successful:

- Chater et al. mixed $NaBH_4$ with $NaNH_2$ in a 1:1 molar ratio and heated at 190 °C for 12 h under argon [53]. For a $NaBH_4$-$NaNH_2$ (1:1 molar ratio) high temperature study, $NaNH_2$-$NaBH_4$ was milled and heated to 220 °C for 1 h, then the mixture annealed at 70 °C for 10 days to reach the low temperature phase. Decomposition temperature was measured using a homebuilt temperature programmed desorption apparatus coupled to a quadrupole mass spectrometer. The sample was heated under a 100 mL/min flow of argon up to 350 °C at a rate of 2 °C/min.
- Wu et al. BM a mixture of $NaNH_2$ and $NaBH_4$ (2:1 molar ratio) under argon at 300 rpm from 1 to 32 h [40]. Decomposition temperature was measured by TG-DTA: heated to 450 °C at 10 °C/min with an Ar purge of 10 ml/min.
- Olsen et al. changed concentrations using a NaCl additive. A mixture of $NaBH_4$ and NaCl with molar ratios 9:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:9 were ball milled under argon at 500 rpm for 24 hrs. Samples were taken out after 2, 6, and 12 h of milling [35]. Decomposition temperature was measured by DSC: heated to 600 °C, at 2 °C/min.
- Ravnsbaek et al. also used NaCl as an additive. $NaBH_4$ with NaCl were BM with respective molar ratios of 0.5:0.5 and 0.75:0.25 under argon 60 times with 2 min of milling followed by 2 min breaks to prevent overheating. After BM, 0.5g of the mixture was transferred to an Al_2O_3 crucible, placed inside a sealed argon filled quartz capillary, and annealed in a furnace at 300 °C for 3 days [36]. Decomposition temperature was measured by Sieverts apparatus: heated to 450 °C at 0.5 °C/min.
- Rude et. al. mixed a 0.1:1 ratio of $NaBF_4$ to $NaBH_4$, BM 15 times under argon with 2 min milling followed by 2 min breaks to cool. Decomposition temperature was measured by TGA/DSC heated to 450 °C at 5 °C/min. [54]

2.5.2 Na Additive Results and Discussion

Sodium (Na) as an additive for $NaBH_4$ has mainly been explored in two forms, $NaNH_2$ and NaCl. As discussed already in this review, the use of chloride-based additives, such as NaCl, produces the same substituted $Na(BH_4)_{1-x}Cl_x$ structure reported for $NiCl_2$, $TiCl_2$ and NaCl, while $NaNH_2$ has shown to produce ammonia emissions. Despite this, the low decomposition and dehydrogenation temperatures for both NaCl and $NaNH_2$ show promise as additives as hydrogen storage materials.

$NaBH_4$-$NaNH_2$ is a composite hydrogen storage material (composed of an amide and a borohydride) which has a theoretical hydrogen storage of more than 7 wt% and the gas product obtained after heating is mainly H_2. $NaBH_4$-$NaNH_2$ was studied because hydrogen generation performances of composite materials such as $NaBH_4$-$NaNH_2$ is considered potentially superior to pure borohydrides or amides. The melting point of $NaNH_2$ is 210 °C and the boiling point is 405 °C. Wu et al. heated $NaNH_2$ to 420 °C and found that $NaNH_2$ decomposes in two stages. The first stage, prior to the melting point,

the weight loss is only about 1.5 wt% [40]. The second stage, after the melting point, the weight loss is 11.6 wt%. Based on TG-DTA data for $NaNH_2$-$NaBH_4$ (2:1 molar ratio), this composite's decomposition mechanism appears to be influence by $NaNH_2$, also having two stages, starting at 124 °C and ending at 420 °C with a total weight loss of 7.52 wt%. Wu et al. found that the thermal decomposition of $NaNH_2$_$NaBH_4$ (2:1) was best controlled below 400 °C [5].

Through a different study, it was found that ball milling a 1:1 ratio of $NaBH_4$ to $NaNH_2$ produced a new complex, $Na_2(BH_4)(NH_2)$. This new compound desorbed hydrogen at about 290 °C after its melting point at about 220 °C [53]. This new compound's high-temperature and low-temperature phase was studied and from the high temperature XRD and differential thermal analysis, $NaNH_2$ was found to react with $NaBH_4$ at 157 °C with good stability up to its melting point (219 °C), with no detectable structure change from 219 °C to 300 °C. Above 300 °C, the dehydrogenation reaction took place [41].

Interestingly, changing the molar ratio from 1:1 to 2:1 of $NaNH_2$/$NaBH_4$ potentially produced $Na_3(BH_4)(NH_2)_2$, which has an onset decomposition temperature of 267 °C, with a 6.85 wt% of hydrogen released by 400 °C [40]. Adding CoNiB to this $Na_3(BH_4)(NH_2)_2$ mixture reduced the onset of dehydrogenation as low as 200 °C with 5.05 wt% of hydrogen released upon heating to 500 °C [53].

Another Na compound, NaCl, was studied by Olsen et al. as an additive for $NaBH_4$. NaCl was chosen for its potential to alter the thermodynamic properties of borohydride materials through anion substitution[35]. The powder X-ray diffraction (PXD) of $NaBH_4$_NaCl with a 1:1 molar ratio showed that NaCl dissolves faster in $NaBH_4$ than vice versa and that 12 hours of milling is sufficient to reach a single phase for mixtures containing less than 50% $NaBH_4$, while more than 50% required 24 hours to reach full homogeneity.

Ravnsbaek et al. found that annealing $NaBH_4$_NaCl after ball milling was better than ball milling alone. Synchrotron radiation powder X-ray diffraction (SR-PXD) data showed that the annealed $NaBH_4$_NaCl dissolved NaCl into $NaBH_4$ at about 240 °C. It was concluded from the SR-PXD data investigating of the decomposition pathway that at higher temperatures (~415 °C), the rate of diffusion is increased, and a homogeneous solid solution is formed before the $NaBH_4$-part decomposed at ~530 °C [36].

Rude et. al. combined a sodium tetrafluoroborate ($NaBF_4$) additive with $NaBH_4$ to make a $NaBH_4$–$NaBF_4$ composite, using PXD to directly observe the substitution of fluorine for the BH_4^- group of $NaBH_4$ [54]. New resonances found in ^{19}F magic-angle spinning NMR supported DFT calculations and confirmed the formation of a complex ion, BF_2H_2, after BM. The H-F exchange destabilized the $NaBH_4$ structure enough to reduce the decomposition temperature to as low as 300 °C. Though other research groups have used different fluoride-based metal additives, the use of Na prevents confusion of the cations in the system and made it possible to observe the direct H-F exchange. Given the dramatic decrease in decomposition it is certainly worth pursuing other fluorine-based metals to determine whether the combination of a F exchange as well as the appropriate metal might enable the $NaBH_4$ system to come closer to approaching DOE's guidelines for H_2 release. Furthermore, it is known that anion substitution can be readily accommodated in borohydrides [55], and there is certainly a need to pursue these additives further with the goal of decreasing the decomposition temperature of $NaBH_4$.

Including the NaCl additive with $NaBH_4$ not only reduced the $NaBH_4$ decomposition to 415 °C, but yielded a H_2 release of 2.6 wt%, which is 90% of the calculated capacity. It was unfortunate that $NaBO_2$ formed during annealing, as this raises questions about cyclability and prevents the mixed material from reaching 100% of the calculated capacity. However, reaching 90% H_2 release is still an impressive feat and is deserving of further exploration. In contrast, $NaNH_2$ as an additive can dehydrogenate at 300 °C with a decomposition temperature of 400 °C, but it produces ammonia emissions, which create additional concerns [31]. It is intriguing that milling $NaNH_2$ with CoNiB reduces the dehydrogenation temperature to 200 °C with 5.05 wt% hydrogen release and no ammonia emissions [30, 31, 53]. $NaBH_4$ containing NaCl and $NaNH_2$ are promising materials compared to mixtures using other additives in this review due to their low decomposition and dehydrogenation temperatures and ability to release a large amount of their H_2. Add to this how promising the addition of CoNiB is to these mixtures, and it is clear that Na additives deserve further exploration.

3. Conclusions

Controlling the decomposition temperature of $NaBH_4$ with additives has met with a wide range of successes, with the decomposition onset temperature ranging from 522 °C with TiF_4 to as low as 300 °C with H-F exchange in $NaBH_4$-$NaBF_4$. Unfortunately, researchers have yet to find a common trend to allow them to destabilize $NaBH_4$ closer to room temperature. Some additive studies have found that fluorides are better than chlorides at weakening $NaBH_4$, especially when it is confirmed that the fluoride can substituted into the BH_4 group, or in additive mixtures involving MgH_2. Ni and Ce additives with fluorides also create a lower decomposition temperature in $NaBH_4$, but not enough work has been done to determine whether this is uniformly true for all metals. It's also unclear if there is a trend where metal nanoparticle additives reduce the decomposition more than their complimentary halogenated metals. For example, Ti nanoparticle additives create a significantly lower decomposition than TiF_4, yet the reverse is not true when comparing Ni nanoparticles to NiF_2.

Researchers have yet to find a reliable method to weaken $NaBH_4$ enough to make it a viable option for H_2 storage, and much more progress is needed to meet DOE's guidelines to release H_2 below 125 °C. It is clear that in order to make a cyclable H_2 storage material of $NaBH_4$, it will be important to find additives that do not create boron derivatives during milling or annealing, a common challenge in the majority of the additives discussed in this review. Our hope is that compiling information on these additives will enable researchers to gain a better understanding of additive incorporation and to determine how a new system might be designed to make $NaBH_4$ a viable H_2 fuel source. It's possible that creating a $NaBH_4$ mixture in-situ would be better than ball milling, or that different types or sizes of nanoparticles could help catalyze $NaBH_4$. There is still a lot that is unknown about $NaBH_4$ and additional research is needed before abandoning it as a potential energy source of the future.

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Competing Interests

The authors have declared that no competing interests exist.

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